CLAIMS

We Claim:

1. A process for polymerizing olefin(s) in the presence of a catalyst system comprising a phenoxide transition metal catalyst compound and a Lewis acid aluminum containing activator, wherein the phenoxide transition metal catalyst compound comprises one or more heteroatom substituted phenoxide ligated Group 3 to 10 transition metal or lanthanide metal compounds, and wherein the Group 3 to 10 transition metal or lanthanide metal of the phenoxide transition metal catalyst compound is bound to the oxygen of the phenoxide group.

2. The process of claim 1 wherein the Lewis acid aluminum containing activator is represented by the formula:

$$AlR_n,$$

where each R is independently a monoanionic ligand, an alkyl group, or represented by the formula ArHal, where ArHal is a halogenated C_6 aromatic or higher carbon number polycyclic aromatic hydrocarbon or aromatic ring assembly in which two or more rings or fused ring systems are joined directly to one another or together, and n is an integer.

3. The process of claim 2 wherein the Lewis acid aluminum containing activator is covalently bonded to a support material.

4. The process of claim 3 wherein the support material contains a functional group selected from the group consisting of hydroxyl, primary alkyl amines, secondary alkyl amines, and combinations thereof.

5. The process of claim 1 wherein the Lewis acid aluminum containing activator is bound to the support material and represented by the formula:

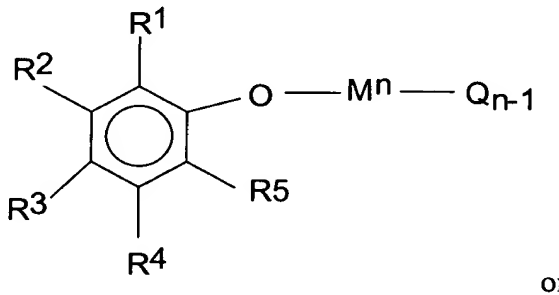
$$(Sup\text{-}E\text{-})_nAl(R)_{4-n}$$

where Sup-E is a Lewis base containing support material or substrate; each R is independently a monoanionic ligand, an alkyl group, or represented by the formula ArHal, where ArHal is a halogenated C_6 aromatic or higher carbon number polycyclic aromatic hydrocarbon or aromatic ring assembly in which two or more rings (or fused ring systems) are joined directly to one another or together ; and n is an integer.

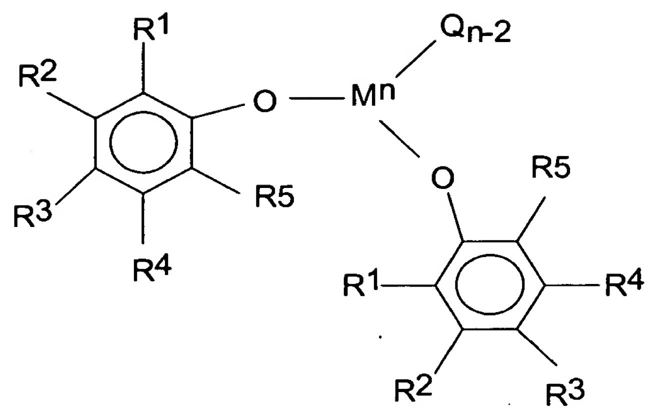
6. The process of claim 2 further comprising another activator selected from the group consisting of alumoxane, modified alumoxane, tri (n-butyl) ammonium tetrakis (pentafluorophenyl) boron, a trisperfluorophenyl boron metalloid precursor, a trisperfluoronaphtyl boron metalloid precursor, polyhalogenated heteroborane anions, trimethylaluminum, triethylaluminum, triisobutylaluminum, tri-n-hexylaluminum, tri-n-octylaluminum, tris (2, 2', 2"- nona-fluorobiphenyl) fluoroaluminate, perchlorates, periodates, iodates and hydrates, (2,2'-bisphenyl-ditrimethylsilicate)•4THF, organo-boron-aluminum compound, silylium salts, dioctadecylmethylammonium-bis(tris(pentafluorophenyl)borane)-benzimidazolide, and combinations thereof.

7. The process of claim 2 wherein the metal component of the Lewis acid aluminum containing activator and the metal component of the phenoxide transition metal catalyst compound are combined in a mole ratio of from about 0.3:1 to about 3:1 respectively.

8. The process of claim 1 wherein the one or more heteroatom substituted phenoxide transition metal compounds may be represented by the following formulae:



or



wherein R^1 to R^5 may be independently hydrogen, a heteroatom containing group or a C_1 to C_{100} group provided that at least one of R^2 to R^5 is a group containing a heteroatom, any of R^1 to R^5 may or may not be bound to the metal M;

O is oxygen;

M is a Group 3 to 10 transition metal or a lanthanide metal,

n is the valence state of M; and

Q is an anionic ligand or a bond to an R group containing a heteroatom which may be any of R^1 to R^5.

9. The process of claim 8 wherein M is a Group 4 metal.

10. The process of claim 8 wherein the heteroatom substituted phenoxide transition metal compound is selected from the group consisting of:

bis(*N*-benzylidene-2-hydroxy-3,5,di-*t*-butylbenzylamine) zirconium(IV) dibenzyl;

bis(*N*-benzylidene-2-hydroxy-3,5,di-*t*-butylbenzylamine) zirconium(IV) dichloride;

bis(2-(2H-benzotriazol-2-yl)-4,6-di-*t*-amylphenoxide)zirconium(IV) dibenzyl;

bis(*N*-benzylidene-2-hydroxy-3,5,di-*t*-butylbenzylamine) titanium(IV) dibenzyl;

bis(2-(2H-benzotriazol-2-yl)-4,6-di-*t*-amylphenoxide)zirconium(IV) dibenzyl;

bis(2-(2H-benzotriazol-2-yl)-4,6-di-*t*-amylphenoxide)zirconium(IV) dichloride;

bis(2-(2H-benzotriazol-2-yl)-4,6-di-*t*-amylphenoxide)zirconium(IV) di(bis(dimethylamide));

bis(2-(2H-benzotriazol-2-yl)-4,6-di-(1',1'-dimethylbenzyl)phenoxide)zirconium(IV) dibenzyl;
bis(2-(2H-benzotriazol-2-yl)-4,6-di-*t*-amylphenoxide)titanium(IV) dibenzyl;
bis(2-(2H-benzotriazol-2-yl)-4,6-di-(1',1'-dimethylbenzyl)phenoxide)titanium(IV) dibenzyl;
bis(2-(2H-benzotriazol-2-yl)-4,6-di-(1',1'-dimethylbenzyl)phenoxide)titanium(IV) dichloride;
bis(2-(2H-benzotriazol-2-yl)-4,6-di-(1',1'-dimethylbenzyl)phenoxide)hafnium(IV) dibenzyl; (*N*-phenyl-3,5-di-(1',1'-dimethylbenzyl)salicylimino)zirconium(IV) tribenzyl.;
bis(4,6-di-t-butyl-2-benzyliminophenoxy)Zr(Benzyl)$_2$; and
bis(4,6-di-t-butyl-2-iso-butyliminophenoxy)Zr(Benzyl)$_2$.

11. The process of claim 8 wherein the heteroatom substituted phenoxide transition metal compound is selected from the group consisting of:
bis(*N*-methyl-3,5-di-*t*-butylsalicylimino)zirconium(IV) dibenzyl;
bis(*N*-ethyl-3,5-di-*t*-butylsalicylimino)zirconium(IV) dibenzyl;
bis(*N-iso*-propyl-3,5-di-*t*-butylsalicylimino)zirconium(IV) dibenzyl;
bis(*N*-*t*-butyl-3,5-di-*t*-butylsalicylimino)zirconium(IV) dibenzyl;
bis(*N*-benzyl-3,5-di-*t*-butylsalicylimino)zirconium(IV) dibenzyl;
bis(*N*-hexyl-3,5-di-*t*-butylsalicylimino)zirconium(IV) dibenzyl;
bis(*N*-phenyl-3,5-di-*t*-butylsalicylimino)zirconium(IV) dibenzyl;
bis(*N*-methyl-3,5-di-*t*-butylsalicylimino)zirconium(IV) dibenzyl;
bis(*N*-benzyl-3,5-di-*t*-butylsalicylimino)zirconium(IV) dichloride;
bis(*N*-benzyl-3,5-di-*t*-butylsalicylimino)zirconium(IV) dipivalate;
bis(*N*-benzyl-3,5-di-*t*-butylsalicylimino)titanium(IV) dipivalate;
bis(*N*-benzyl-3,5-di-*t*-butylsalicylimino)zirconium(IV) di(bis(dimethylamide));
bis(*N-iso*-propyl-3,5-di-*t*-amylsalicylimino)zirconium(IV) dibenzyl;
bis(*N-iso*-propyl-3,5-di-*t*-octylsalicylimino)zirconium(IV) dibenzyl;
bis(*N-iso*-propyl-3,5-di-(1',1'-dimethylbenzyl)salicylimino)zirconium(IV) dibenzyl;
bis(*N-iso*-propyl-3,5-di-(1',1'-dimethylbenzyl)salicylimino)titanium(IV) dibenzyl;
bis(*N-iso*-propyl-3,5-di-(1',1'-dimethylbenzyl)salicylimino)hafnium(IV) dibenzyl;

bis(*N-iso*-butyl-3,5-di-(1',1'-dimethylbenzyl)salicylimino)zirconium(IV) dibenzyl;
bis(*N-iso*-butyl-3,5-di-(1',1'-dimethylbenzyl)salicylimino)zirconium(IV) dichloride;
bis(*N*-hexyl-3,5-di-(1',1'-dimethylbenzyl)salicylimino)zirconium(IV) dibenzyl;
bis(*N*-phenyl-3,5-di-(1',1'-dimethylbenzyl)salicylimino)zirconium(IV) dibenzyl;
bis(*N-iso*-propyl-3,5-di-(1'-methylcyclohexyl)lsalicylimino)zirconium(IV) dibenzyl;
bis(*N*-benzyl-3-*t*-butylsalicylimino)zirconium(IV) dibenzyl;
bis(*N*-benzyl-3-triphenylmethylsalicylimino)zirconium(IV) dibenzyl;
bis(*N-iso*-propyl-3,5-di-trimethylsilylsalicylimino)zirconium(IV) dibenzyl;
bis(*N-iso*-propyl-3-(phenyl)salicylimino)zirconium(IV) dibenzyl;
bis(*N*-benzyl-3-(2',6'-di-*iso*-propylphenyl)salicylimino)zirconium(IV) dibenzyl;
bis(*N*-benzyl-3-(2',6'-di-phenylphenyl)salicylimino)zirconium(IV) dibenzyl;
bis(*N*-benzyl-3-*t*-butyl-5-methoxysalicylimino)zirconium(IV) dibenzyl;
bis(2-(2H-benzotriazol-2-yl)-4,6-di-*t*-amylphenoxide)zirconium(IV) dibenzyl;
bis(2-(2H-benzotriazol-2-yl)-4,6-di-*t*-amylphenoxide)zirconium(IV) dichloride;
bis(2-(2H-benzotriazol-2-yl)-4,6-di-*t*-amylphenoxide)zirconium(IV) di(bis(dimethylamide));
bis(2-(2H-benzotriazol-2-yl)-4,6-di-(1',1'-dimethylbenzyl)phenoxide)zirconium(IV) dibenzyl;
bis(2-(2H-benzotriazol-2-yl)-4,6-di-*t*-amylphenoxide)titanium(IV) dibenzyl;
bis(2-(2H-benzotriazol-2-yl)-4,6-di-(1',1'-dimethylbenzyl)phenoxide)titanium(IV) dibenzyl;
bis(2-(2H-benzotriazol-2-yl)-4,6-di-(1',1'-dimethylbenzyl)phenoxide)titanium(IV) dichloride;
bis(2-(2H-benzotriazol-2-yl)-4,6-di-(1',1'-dimethylbenzyl)phenoxide)hafnium(IV) dibenzyl;
(*N*-phenyl-3,5-di-(1',1'-dimethylbenzyl)salicylimino)zirconium(IV) tribenzyl
(*N*-(2',6'-di-*iso*-propylphenyl)-3,5-di-(1',1'-dimethylbenzyl)salicylimino)zirconium(IV) tribenzyl;
(*N*-(2',6'-di-*iso*-propylphenyl)-3,5-di-(1',1'-dimethylbenzyl)salicylimino)titanium(IV) tribenzyl; and

(*N*-(2',6'-di-*iso*-propylphenyl)-3,5-di-(1',1'-dimethylbenzyl)salicylimino)zirconium(IV) trichloride.

12. The process of claim 1 wherein the process is a continuous gas phase process.

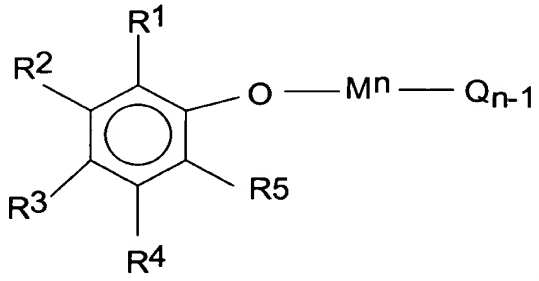
13. The process of claim 1 wherein the process is a continuous slurry phase process.

14. The process of claim 1 wherein the olefin(s) is ethylene or propylene.

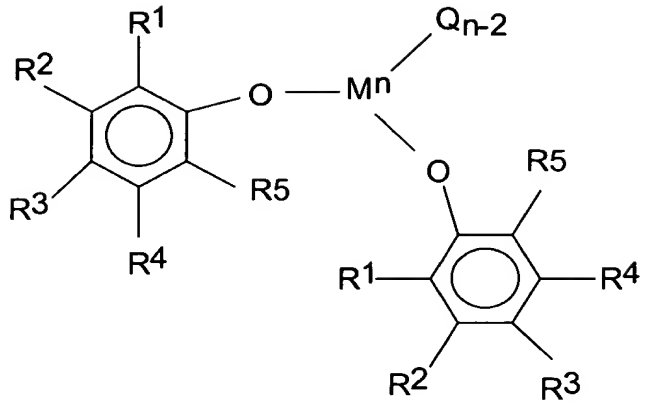
15. The process of claim 1 wherein the olefins are ethylene and at least one other monomer having from 3 to 20 carbon atoms.

16. A supported catalyst system comprising a phenoxide transition metal catalyst compound an activator and a support material wherein:

a) the phenoxide transition metal catalyst compound is represented by the formulae:



or



where R^1 to R^5 may be independently hydrogen, a heteroatom containing group or a C_1 to C_{100} group provided that at least one of R^2 to R^5 is a group containing a heteroatom, any of R^1 to R^5 may or may not be bound to the metal M;

O is oxygen;

M is a Group 3 to 10 transition metal or a lanthanide metal,

n is the valence state of M; and Q is an anionic ligand or a bond to an R group containing a heteroatom which may be any of R^1 to R^5; and wherein

b) the activator is a Lewis acid aluminum containing activator represented by the formula:

$$AlR_n,$$

where each R is independently a monoanionic ligand, an alkyl group, or represented by the formula ArHal, where ArHal is a halogenated C_6 aromatic or higher carbon number polycyclic aromatic hydrocarbon or aromatic ring assembly in which two or more rings (or fused ring systems) are joined directly to one another or together, and n is an integer.

17. The supported catalyst system of claim 16 where the support material contains surface hydroxyl groups.

18. The supported catalyst system of claim 17 wherein the aluminum is covalently bonded to the support material.

19. The supported catalyst system of claim 18 wherein the Lewis acid aluminum containing activator is bound to the support material and represented by the formula:

$$(\text{Sup-E-})_n\text{Al}(\text{R})_{4-n} \qquad \text{(IV)}$$

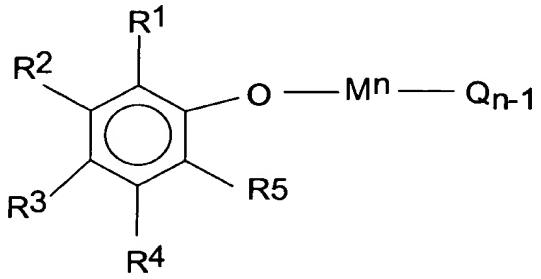
where Sup-E is a Lewis base containing support material or substrate; each R is independently a monoanionic ligand, an alkyl group, or represented by the formula ArHal, where ArHal is a halogenated C_6 aromatic or higher carbon number polycyclic aromatic hydrocarbon or aromatic ring assembly in which two or more rings (or fused ring systems) are joined directly to one another or together ; and n is an integer.

20. A method of preparing a catalyst system comprising:

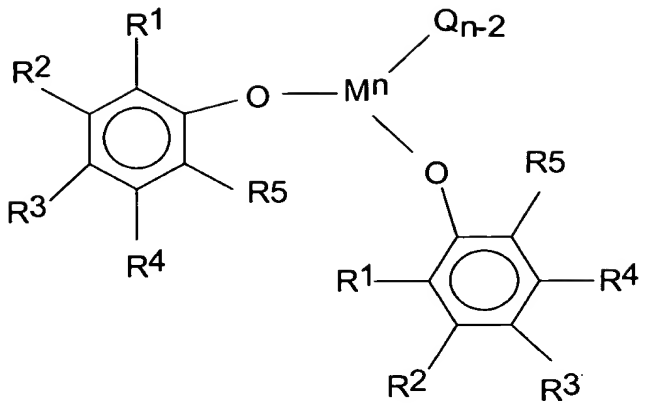
a) contacting a phenoxide transition metal catalyst compound and a Lewis acid containing activator in a liquid to form a mixture;

b) contacting the mixture of step a) with a support material.

21. The method of claim 19 wherein the phenoxide transition metal catalyst compound is represented by the formulae:



or



where R^1 to R^5 may be independently hydrogen, a heteroatom containing group or a C_1 to C_{100} group provided that at least one of R^2 to R^5 is a group containing a heteroatom, any of R^1 to R^5 may or may not be bound to the metal M;

O is oxygen;

M is a Group 3 to 10 transition metal or a lanthanide metal,

n is the valence state of M; and Q is an anionic ligand or a bond to an R group containing a heteroatom which may be any of R^1 to R^5; and wherein

b) the activator is a Lewis acid aluminum containing activator represented by the formula:

$$AlR_n,$$

where each R is independently a monoanionic ligand, an alkyl group, or represented by the formula ArHal, where ArHal is a halogenated C_6 aromatic or higher carbon number polycyclic aromatic hydrocarbon or aromatic ring assembly in which two or more rings (or fused ring systems) are joined directly to one another or together, and n is an integer, preferably 3.

22. The method of claim 19 where the support material contains surface hydroxyl groups.

23. The method of claim 19 wherein the Lewis acid aluminum containing activator is bound to the support material and represented by the formula:

$$(Sup\text{-}E\text{-})_nAl(R)_{4-n} \qquad (IV)$$

where Sup-E is a Lewis base containing support material or substrate; each R is independently a monoanionic ligand, an alkyl group, or represented by the formula ArHal, where ArHal is a halogenated C_6 aromatic or higher carbon number polycyclic aromatic hydrocarbon or aromatic ring assembly in which two or more rings (or fused ring systems) are joined directly to one another or together ; and n is an integer, preferably n is 1, 2 or 3.